

The vibrational spectra of 2-, 3- and 4-acetylpyridine

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In infrared absorption spectra in the region $4000-50\text{ cm}^{-1}$ and the laser Raman spectra in pure liquid state have been studied for 2-, 3- and 4-acetylpyridine. An essentially complete assignment of the observed frequencies is given.

1 INTRODUCTION

In extension of the earlier study of the vibrational spectra of some substituted pyridines (Medhi & Mukherjee 1965, Medhi 1965, 1972), the infrared and Raman spectra of 2-, 3- and 4- acetylpyridine have been investigated in the pure liquid state. A few characteristic infrared bands were reported by Katritzky & Gardner (1958), Katritzky & Hands (1958) and Katritzky *et al* (1958) together with their assignments in the case of the three isomers of acetylpyridine in solution in chloroform, and by Hideyo Shindo (1957) in the case of 2-acetylpyridine. There appears to be no previous report on the Raman spectra of those molecules.

The present paper deals with a detailed study of the infrared and Raman spectra of the three isomeric acetylpyridines. An essentially complete assignment of the observed vibrational frequencies, based on the state of polarization of the Raman lines and comparison with the assignments proposed for the related molecules (Green *et al* 1963, Spinner 1963, Long & George 1963, Berezin & Elkin 1973, Mross & Zundel 1970), is presented.

2. EXPERIMENTAL

The compounds used in this work were obtained from Koch-Light Laboratories Ltd., England. The samples were purified by fractional distillation, and in each case the proper fraction distilled at a constant temperature was collected for use in the experiment.

The infrared absorption spectra in the region $4000-400\text{ cm}^{-1}$ were recorded on a Beckman IR-12 spectrophotometer. The calibration of the instrument was checked by the spectrum of a polystyrene film. The far infrared spectra in the range $500-50\text{ cm}^{-1}$ were scanned in the pure liquid state using a Perkin-Elmer Model 180 spectrophotometer and a 0.1 mm polyethylene cell. The Raman spectra were taken on a Cary Model 82 laser Raman spectrophotometer and a Spex Ramacomp 5. The spectra were excited by either the 4880 Å (60 mW) or 5145 Å (300 mW) line of an argon ion laser. The polarization of the Raman lines was

measured for two different mutually perpendicular orientations of the analyser in the scattered beam, while the plane of polarization of the laser beam was kept fixed.

3. RESULTS AND DISCUSSION

The observed infrared frequencies and Raman shifts of the three compounds together with their approximate intensities and assignments are listed in table 1-3. For comparison the fundamental frequencies of pyridine (Wilmshurst &

Table 1. Vibrational frequencies and assignments for 2-acetylpyridine

Infrared (cm ⁻¹)	Raman (cm ⁻¹)	Assignment
160 (w)	163 (2) dp	a'' fundamental
215 (w)		a'' fundamental, —C-CH ₃ Out-of plane deformation
362 (w)	366 (1) p	a' fundamental
395 (sh)		a' fundamental, —C-CH ₃ in-plane deformation ~
409 (w)		a'' and a'' fundamentals, —C=O out-of-plane deformation
482 (vw)	~ 492 (0)	a'' fundamental
590 (vs)	590 (0) p	a' and a' fundamentals, —C=O in-plane deformation ✓
622 (m)	622 (2) p	a' fundamental
700 (w)		a'' fundamental
740 (s)	750 (3) p	a' fundamental
779 (vs)	~ 783 (0)	a'' fundamental
903 (w)		a'' fundamental
	953 (1) p	a' fundamental, —CH ₃ in-plane rocking //
954 (s)		a'' fundamental
996 (s)	995 (10) p	a' fundamental
1018 (m)		a'' fundamental, —CH ₃ out-of-plane rocking //
1043 (s)	1044 (5) p	a' fundamental
1086 (m)	1086 (1) p	a' fundamental
1100 (vs)	1101 (1) p	a' fundamental
1146 (m)	1150 (0) p	a' fundamental
1238 (vs)	1238 (2) p	a' fundamental, —C-CH ₃ stretching ✓

Table 1 (contd.)

Infrared (cm ⁻¹)	Raman (cm ⁻¹)	Assignment
1281 (vs)	1282 (2) p	a' fundamental
1296 (vs)	1296 (2) p	a' fundamental
1357 (vs)		a' fundamental, —CH ₃ symmetric deformation
1421 (s)		a' fundamental
1437 (vs)	1437 (2) p	a' and a'' fundamentals, —CH ₃ asymmetric deformation
1465 (s)		a' fundamental
1560 (m)		2 × 779 = 1558 (A')
1568 (s)	1569 (1) p	a' fundamental
1585 (vs)	1585 (5) p	a' fundamental
1619 (w)		622 + 996 = 1618 (A')
1659 (w)		622 + 1043 = 1665 (A')
1702 (vs)	1697 (5) p	a' fundamental, —C=O stretching ✓
1826 (vw)		590 + 1238 = 1828 (A')
1870 (w)		590 + 1281 = 1871 (A')
1905 (w)		2 × 954 = 1908 (A')
1969 (w)		954 + 1018 = 1972 (A')
2107 (vw)		954 + 1146 = 2100 (A'')
2190 (vw)		954 + 1238 = 2192 (A'')
2258 (vw)		954 + 1281 = 2235 (A'')
2309 (w)		740 + 1568 = 2308 (A')
2369 (vw)		779 + 1585 = 2364 (A'')
2444 (vw)		740 + 1702 = 2442 (A')
2480 (vw)		779 + 1702 = 2481 (A'')
2518 (vw)		1238 + 1281 = 2519 (A')
2537 (w)		1100 + 1437 = 2537 (A' or A'')
2584 (vw)		996 + 1585 = 2581 (A')
2653 (w)		1296 + 1357 = 2653 (A')
2670 (w)		1100 + 1568 = 2668 (A')
2700 (vw)		1281 × 1421 = 2702 (A')
2758 (vw)		1296 + 1465 = 2761 (A')

Table 1 (contd.)

Infrared (cm ⁻¹)	Raman (cm ⁻¹)	Assignment
2816 (w)		1238 + 1585 = 2823 (A')
2864 (w)		2 × 1437 = 2874 (A')
2925 (m)	2924 (2) p	a' and a'' fundamentals, —CH ₃ symmetric stretching
2982 (sh) } 3011 (m) }	3010 (1) p	a' and a'' fundamentals, —CH ₃ asymmetric stretching
3060 (m)	3062 (2) p	a', a', a' and a' fundamentals
3136 (m)	3138 (0) p	2 × 1568 = 3136 (A')
3166 (w)	3168 (0) p	2 × 1585 = 3170 (A')
3388 (w)		2 × 1702 = 3404 (A')

(s)=strong; (m)=medium; (w)=weak; (v)=very; (sh)=shoulder;
p=polarized; dp=depolarized.

Table 2. Vibrational frequencies and assignments for 3-acetylpyridine

Infrared (cm ⁻¹)	Raman (cm ⁻¹)	Assignment
162 (w)	164 (1) dp	a'' fundamental
221 (w)		a'' fundamental, —C-CH ₃ out-of-plane deformation
366 (w)	168 (0) p	a' fundamental
383 (w)		a' fundamental, —C-CH ₃ in-plane deformation
406 (w)		a'' and a'' fundamentals, —C=O out-of-plane deformation
472 (w)		a'' fundamental
590 (vs)	591 (0) p	a' and a' fundamentals, —C=O in plane deformation
623 (s)	624 (1) p	a' fundamental
704 (vs)		a'' fundamental
749 (m)	751 (2) p	a' fundamental
809 (vs)		a'' fundamental
928 (w)		a'' fundamental
	957 (0) p	a' fundamental, —CH ₃ in-plane rocking
958 (vs)		a'' fundamental

Table 2 (contd).

Infrared (cm ⁻¹)	Raman (cm ⁻¹)	Assignment
1023 (vs)		a'' fundamental, —CH ₃ out-of-plane rocking
1034 (sh)	1035 (10) p	a' fundamental
1081 (sh)	1078 (0) p	a' fundamental
1093 (s)	1091 (sh)	a' fundamental
1118 (s)		a' fundamental
1127 (m)		a' fundamental
1195 (s)	1195 (1)	a' fundamental, —C-CH ₃ stretching
1242 (s)	1243 (0) p	a' fundamental
1274 (vs)	1272 (1)	a' fundamental
1325 (sh)		623 + 704 = 1327 (A'')
1462 (vs)		a' fundamental, —CH ₃ symmetric deformation
1420 (vs)	1417 (0)	a' fundamental
1470 (m)		a' and a'' fundamentals, —CH ₃ asymmetric deformation
1478 (m)	1480 (0)	a' fundamental
1574 (s)	1574 (sh)	a' fundamental
1587 (vs)	1586 (3) p	a' fundamental
1629 (w)		590 + 1034 = 1624 (A')
1653 (w)		704 + 958 = 1662 (A')
1690 (vs)	1686 (3) p	a' fundamental, —C=O stretching
1779 (w)		590 + 1195 = 1785 (A')
1861 (w)		590 + 1274 = 1864 (A')
1925 (w)		809 + 1118 = 1927 (A'')
1952 (w)		590 + 1162 = 1952 (A')
2021 (w)		749 + 1274 = 2023 (A')
2111 (vw)		749 + 1362 = 2111 (A')
2229 (vw)		809 + 1420 = 2229 (A'')
2325 (vw)		958 + 1362 = 2320 (A'')
2389 (vw)		2 × 1195 = 2390 (A')
2441 (vw)		958 + 1478 = 2436 (A'')

Table 2 (contd).

Infrared (cm^{-1})	Raman (cm^{-1})	Assignment
2513 (vw)		$1093 + 1420 = 2513$ (A')
2543 (vw)		$2 \times 1274 = 2548$ (A')
2605 (vw)		$1242 + 1362 = 2604$ (A')
2645 (vw)		$958 + 1690 = 2648$ (A'')
2856 (w)		$1274 + 1587 = 2861$ (A')
2925 (m)	2921 (2) p	a' fundamental, —CH ₃ symmetric stretching
2972 (m)	2968 (0)	a' and a'' fundamentals, —CH ₃ asymmetric stretching
3011 (m)	3006 (0)	
3053 (m)		a' fundamental
	3059 (2) p	a' and a' fundamentals
3089 (m)	3089 (sh)	a' fundamental
3168 (w)		$2 \times 1587 = 3174$ (A')
3367 (m)		$2 \times 1690 = 3380$ (A')

Table 3. Vibrational frequencies and assignments for 4-acetylpyridine

Infrared (cm^{-1})	Raman (cm^{-1})	Assignment
158 (w)	160 (1) dp	a'' fundamental
219 (w)		a'' fundamental, —C-CH ₃ out-of-plane deformation
358 (w)	364 (1) p	a' fundamental
417 (w)		a'' and a' fundamentals, —C=O out-of-plane deformation
465 (vw)		a'' fundamental
590 (vs)	589 (0) p	a' and a' fundamentals, —C=O in-plane deformation
601 (vs)	603 (0)	a' fundamental
664 (w)	666 (2) dp	a'' fundamental
736 (w)	739 (3) p	a' fundamental
817 (vs)		a'' fundamental
875 (w)		a'' fundamental
	962 (1) p	a' fundamental, —CH ₃ in-plane rocking

Table 3 (contd.)

Infrared (cm ⁻¹)	Raman (cm ⁻¹)	Assignment
963 (s)		a'' fundamental
993 (s)	993 (10) p	a' fundamental
1021 (m)		a'' fundamental, —CH ₃ out-of-plane rocking
1033 (s)	1064 (1) p	a' fundamental
1083 (m)	1084 (3) p	a' fundamental
1115 (w)		a' fundamental
1220 (m)	1214 (2) p	a' fundamental
1253 (s)		a' fundamental, —C-CH ₃ stretching
1267 (vs)	1267 (2) p	a' fundamental
1324 (m)	1324 (0)	a' fundamental
1362 (vs)		a' fundamental, —CH ₃ symmetric deformation
1410 (vs)		a' fundamental
1423 (sh)		a' and a'' fundamentals, —CH ₃ asymmetric deformation
1494 (m)	1492 (1) p	a' fundamental
1557 (s)	1556 (0)	a' fundamental
1597 (m)	1596 (2) p	a' fundamental
1627 (w)		601 + 1021 = 1622 (A'')
1656 (m)		590 + 1063 = 1653 (A')
1696 (vs)	1694 (3) p	a' fundamental, —C=O stretching
1774 (sh)		817 + 963 = 1780 (A')
1854 (w)		590 + 1267 = 1857 (A')
1949 (w)		590 + 1362 = 1952 (A')
2001 (w)		590 + 1410 = 2000 (A')
2097 (vw)		601 + 1494 = 2095 (A')
2149 (vw)		590 + 1557 = 2147 (A')
2177 (vw)		817 + 1362 = 2179 (A'')
2209 (vw)		993 + 1220 = 2213 (A')
2315 (w)		817 + 1494 = 2311 (A'')
2385 (w)		1021 + 1362 = 2383 (A'')

Table 3 (contd.)

Infrared (cm^{-1})	Raman (cm^{-1})	Assignment
2445 (w)		1083 + 1362 = 2445 (A')
2527 (vw)		2 + 1267 = 2534 (A')
2585 (vw)		1267 + 1324 = 2591 (A')
2625 (vw)		1267 + 1362 = 2629 (A')
2655 (w)		1063 + 1597 = 2660 (A')
2707 (vw)		1220 + 1494 = 2714 (A')
2769 (vw)		1410 + 1362 = 2772 (A')
2860 (w)		1267 + 1597 = 2864 (A')
2887 (w)		1324 + 1557 = 2881 (A')
2923 (m)	2922 (2) p	a' fundamental, - CH_3 symmetric stretching
2972 (w)	2972 (0) p	a' fundamental, - CH_3 asymmetric stretching
2987 (w)		1423 + 1557 = 2980 (A' or A'')
3009 (m)	3010 (sh)	a'' fundamental, - CH_3 asymmetric stretching
3031 (m)	3031 (0)	a' fundamental
3047 (m)	3050 (sh)	a' fundamental
3066 (m)	3066 (2) p	a' fundamental
3082 (m)		a' fundamental
3152 (w)		1557 + 1597 = 3154 (A')
3381 (m)		2 + 1696 = 3392 (A')

Bernstein 1957) and 2-, 3- and 4-acetylpyridine are collected in table 4. The laser Raman spectra and the portions of the infrared spectra ($3500\text{--}500\text{ cm}^{-1}$) in the liquid state are reproduced in Figures 1(a), (b) and (c) and Figures 2(a), (b) and (c) respectively.

Each of the three isomeric acetylpyridine molecules is assumed to have the C_s symmetry, and the forty-two normal modes of vibration are distributed amongst the symmetry species as follows :

$$28a' + 14a''$$

According to the selection rules all the vibrations are active both in the infrared and Raman spectra. While the species a' should give rise to polarized Raman lines, the species a'' will have depolarized Raman lines.

Table 4. Fundamental vibrational frequencies of pyridine, 2-, 3- and 4-acetylpyridine

[The internal vibrations of the acetyl group are not included]

Symmetry species	Mode No. (Wilson 1934)	Wavenumber (cm ⁻¹)			
		Pyridine	2-Acetyl- pyridine	3-Acetyl- pyridine	4-Acetyl pyridine
a'	1	992	995	1035	993
	2	3054	3062	3059	3066
	6a	605	(590)	(591)	(589)
	8a	1583	1585	1586	1596
	9a	1218	1150	1127	1214
	12	1030	750	751	739 ✓
	13	(3054)	1086	1093	1084
	18a	1668	1644	1678	1664
	19a	1482	1465	1478	1494
	20a	3036	(3062)	(3059)	3017
	3	(1218)	1282	1242	1267
	6b	652	622	624	601
	7b	(3036)	(3062)	3053	3031
	8b	1572	1569	1574	1557
	14	1375	1296	1272	1324
	15	1148	1101	1118	1115
	18b	1085	366	368	364
	19b	1439	1421	1420	1410
	20b	3083	(3062)	3089	3.82
a''	10a	886	---	---	---
	16a	374	(409)	(405)	(417)
	17a	981	954	958	963
	4	749	700	704	666
a''	5	942	903	928	875
	10b	(886)	779	809	817
	11	700	482	472	465
	16b	405	163	164	160

() Frequency assigned more than once.

--- Frequency not observed.

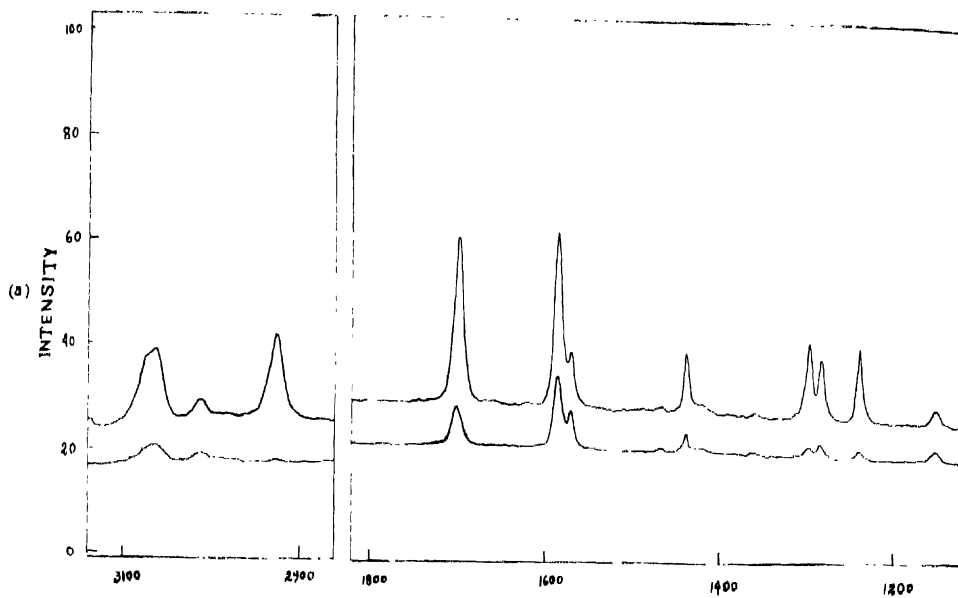


Fig. 1(a)

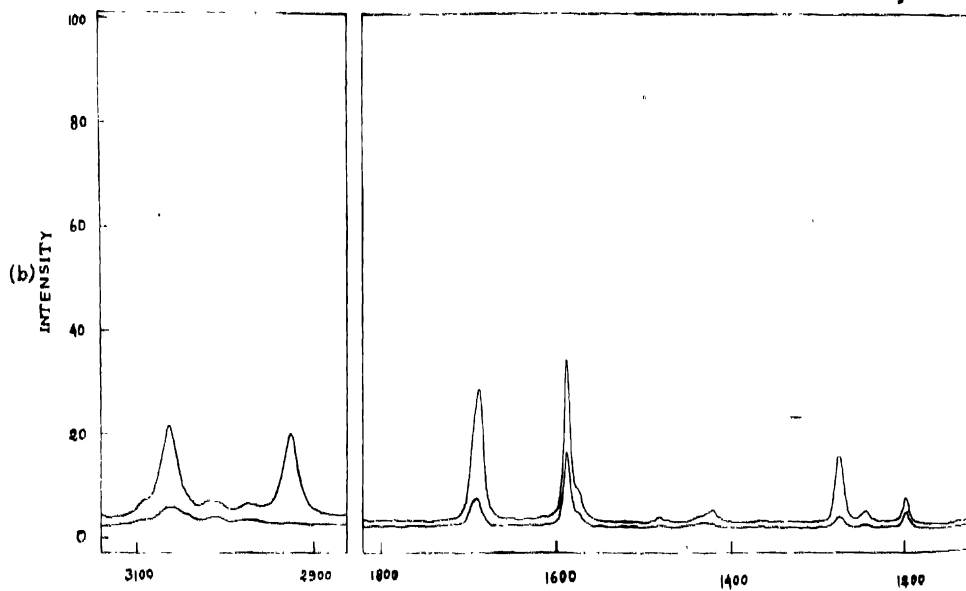


Fig. 1(b)

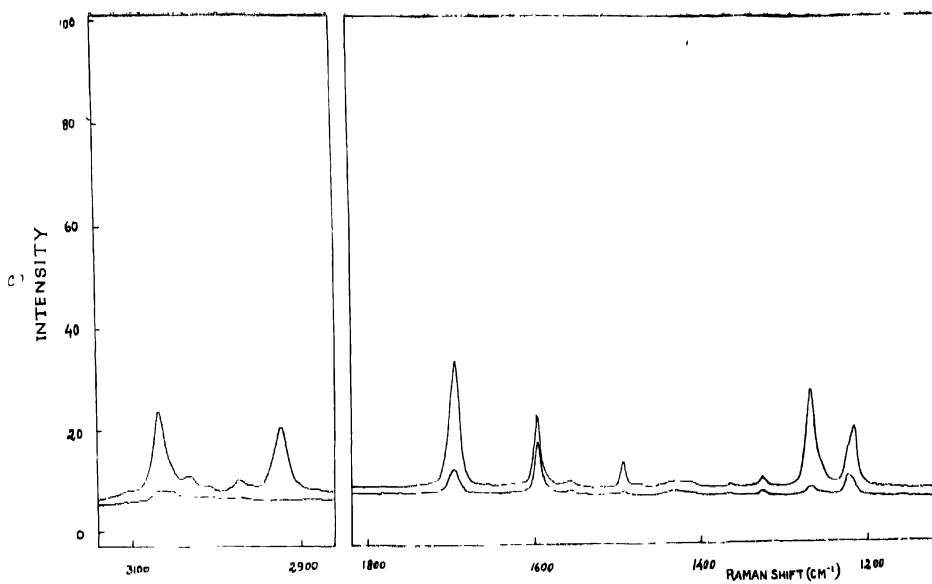


Fig. 1(c)

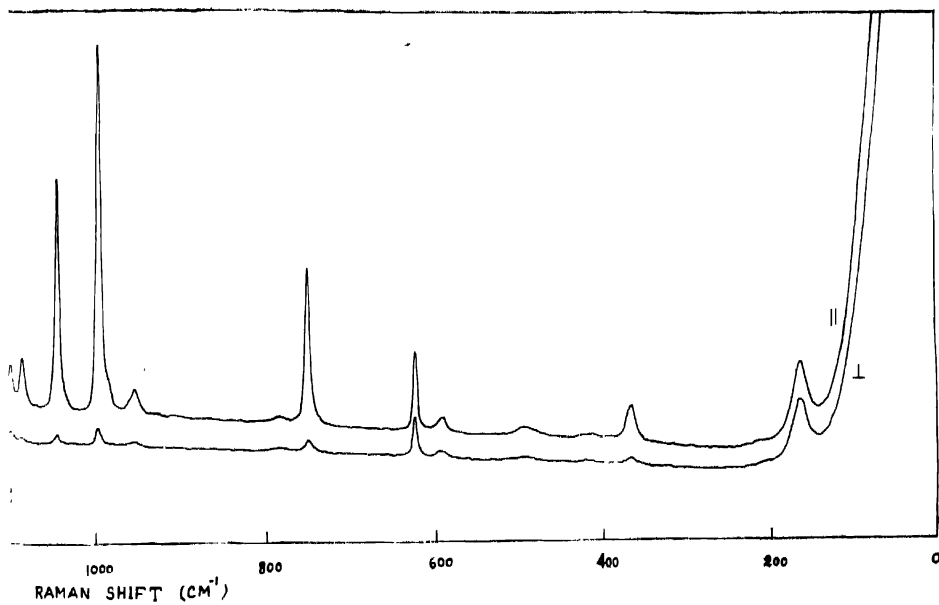


Fig. 2(a)

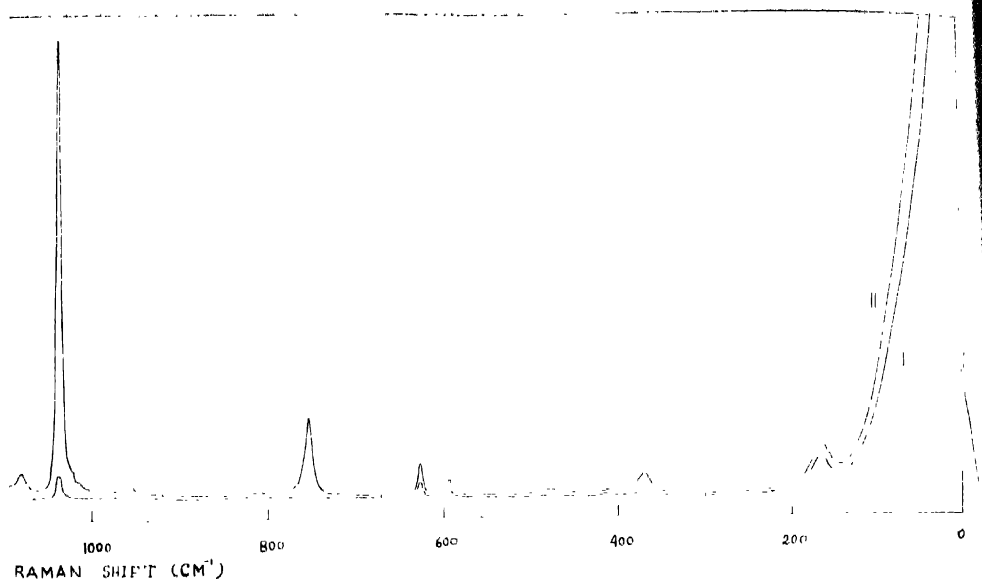


Fig. (2b)

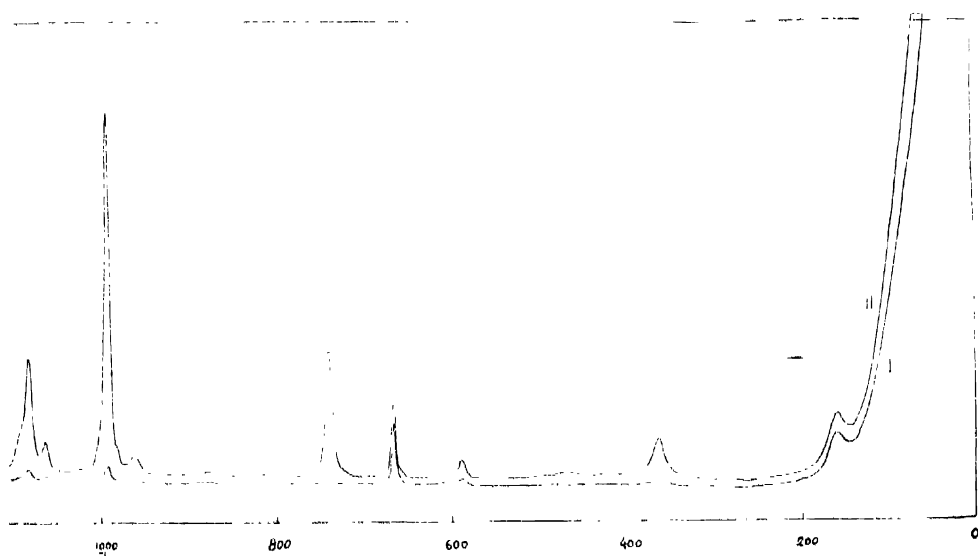


Fig. (2c)

Species a'

Of the nineteen a' modes of vibration that can be derived from pyridine, four involve essentially stretching of the C-H bonds. The polarized Raman line observed at 3062 cm^{-1} with its infrared counterpart at 3060 cm^{-1} in 2-acetylpyridine, and the Raman shift at 3059 cm^{-1} and the infrared bands at 3053 and 3089 cm^{-1} in 3-acetylpyridine, and the Raman lines at 3031 and 3066 cm^{-1} and the infrared frequencies at 3047 and 3082 cm^{-1} in 4-acetylpyridine are assigned to the C-H valence oscillations. The pairs of well-resolved bands at 1569 and 1585 cm^{-1} , 1587 and 1574 cm^{-1} , and 1597 and 1557 cm^{-1} in the case of the three molecules respectively are readily identified with the highest ring stretching frequencies. The next highest C-C (C-N) stretching modes belonging to the a' class are expected in the 1400 cm^{-1} region, and they may be represented by the infrared frequencies at 1421 and 1465 cm^{-1} , 1420 and 1478 cm^{-1} , and 1410 and 1494 cm^{-1} observed in the three isomers of acetylpyridine respectively. The Raman spectra of 2-, 3- and 4-acetylpyridine show very intense and highly polarized lines at 995 , 1035 and 993 cm^{-1} respectively and they are unambiguously assigned to the ring breathing mode. The remaining mode being derived primarily from carbon stretching may be attributed to the observed frequencies at 1296 , 1272 and 1324 cm^{-1} in 2-, 3- and 4-acetylpyridine respectively.

In monosubstituted pyridines there are four planar modes which are more substituent-sensitive. Thus the polarized Raman lines at 366 , 590 , 750 and 1086 cm^{-1} in 2-acetylpyridine, 364 , 589 , 739 and 1084 cm^{-1} in 4-acetylpyridine and 368 , 591 and 751 cm^{-1} and the infrared band of medium strength at 1093 cm^{-1} in 3-acetylpyridine may be assigned to these modes. The remaining fundamentals belonging to this class are identified with the polarized Raman lines observed at 622 , 1044 , 1101 , 1150 and 1282 cm^{-1} in 2-acetylpyridine, 624 and 1078 cm^{-1} and the infrared bands at 1118 , 1127 and 1242 cm^{-1} in 3-acetylpyridine, and the polarized Raman lines at 1064 , 1214 and 1267 cm^{-1} and the infrared bands at 601 and 1115 cm^{-1} in 4-acetylpyridine.

Species a''

In the a'' class there would be eight pyridine-like modes. The Raman lines at 163 , 164 and 160 cm^{-1} in the case of 2-, 3- and 4-acetylpyridine respectively are observed to be depolarized. The corresponding infrared absorption frequencies occur at 160 , 162 and 158 cm^{-1} . They may be associated with the lowest non-planar ring angle deformation mode which is sensitive to the substituent. The remaining a'' fundamentals are assigned to the observed frequencies at 409 , 482 , 700 , 779 , 903 and 954 cm^{-1} in 2-acetylpyridine, 405 , 472 , 704 , 809 , 928 and 958 cm^{-1} in 3-acetylpyridine, and 417 , 465 , 664 , 817 , 875 and 963 cm^{-1} in 4-acetylpyridine. Those assignments are in close agreement with those made in the case of other monosubstituted pyridines (Green *et al* 1963). One fundamental belonging to

this class being either very weak or coincident with some other fundamental is left unassigned.

The internal vibrations of the acetyl group

Besides these twenty-seven pyridyl frequencies, there would be fifteen other modes arising from the internal motions of the acetyl group. They may be classified as follows :

- (i) One C = O stretch (α') and two C = O deformations—one in-plane (α') and one out-of-plane (α'').
- (ii) One CH₃ symmetric (α') and two CH₃ asymmetric (α' , α'') stretches, one CH₃ symmetric (α') and two CH₃ asymmetric (α' , α'') deformations, two CH₃ rocking modes—one in-plane (α') and one out-of-plane (α''), and one torsional mode (α'') of the CH₃ group.
- (iii) One C-CH₃ stretch (α'), one C-CH₃ in-plane deformation (α') and one C-CH₃ out-of-plane deformation (α'').

The C = O stretching frequencies are readily identified. The intense infrared band at 590 cm⁻¹ observed in the case of the three molecules is assigned to the C = O in-plane bending mode, whilst the C = O out-of-plane deformation may be responsible for the infrared frequencies at 409, 405 and 417 cm⁻¹, which are already assigned to another fundamental, in the case of 2-, 3- and 4-acetylpyridine respectively. These assignments are made in comparison with those proposed for acetone (Harris & Levin 1972, Allkins & Lippincott 1969, Cossee & Schachtschneider 1966). While the CH₃ stretching and deformation frequencies are easily assigned, there remains some uncertainty in the assignment of the rocking modes of the CH₃ group. The observed infrared bands at 1018, 1023 and 1021 cm⁻¹ in 2-, 3- and 4-acetylpyridine respectively are assigned to the out-of-plane rocking mode of the methyl group, and the in-plane rocking mode may be represented by the Raman shifts at 953, 957 and 962 cm⁻¹. The torsional mode of the CH₃ group is, however, left unidentified. The C-CH₃ stretching and in-plane and out-of-plane bending modes are assigned respectively to the frequencies at 1238 395 and 215 cm⁻¹ in 2-acetylpyridine and 1195 383 and 221 cm⁻¹ in 3-acetylpyridine. In the case of the 4-isomer while the C-CH₃ stretching and out-of-plane bending modes are identified with the observed infrared bands at 1253 and 219 cm⁻¹ respectively, the in-plane deformation frequency is either very weak or coincident with the fundamental at 355 cm⁻¹.

Overtones and combination bands

In addition to the above fundamental frequencies, other weak bands are observed both in the infrared and Raman spectra. They may be assigned as overtones or combination bands of the fundamental frequencies.

REFERENCES

- Allkins J. R. & Lippincott E. R. 1969. *Spectrochim. Acta* **25A**, 761.
Berezin V. I. & Elkin M. D. 1973. *Optics and Spectroscopy* **34**, 395.
Cossee P. & Schachtschneider J. H. 1966. *J. Chem. Phys.* **44**, 97.
Green J. H. S., Kynaston W. & Paisloy H. M. 1963. *Spectrochim. Acta* **19**, 549.
Harris W. C. & Levin I. W. 1972. *J. Mol. Spectroscopy* **43**, 117.
Hideyo Shindo 1957. *Pharm. Bull. (Tokyo)* **5**, 472.
Katritzky A. R. & Gardner J. N. 1958. *J. Chem. Soc.* 2198.
Katritzky A. R. & Hands A. R. 1958. *J. Chem. Soc.* 2202.
Katritzky A. R., Hands A. R. & Jones R. A. 1958. *J. Chem. Soc.* 3165.
Long D. A. & George W. O. 1963. *Spectrochim. Acta* **19**, 1777.
Medhi K. C. & Mukherjee D. K. 1965. *Spectrochim. Acta* **21**, 895.
Medhi K. C. 1965. *Optika i Spektroskopiya* **19**, 49.
Medhi K. C. 1972. *Ind. J. Phys.* **46**, 300.
Mross W. D. & Zundol G. 1970. *Spectrochim. Acta* **26A**, 1097.
Spinner E. 1963. *J. Chem. Soc.* 3860.
Wilmschurst J. K. & Bernstein H. J. 1957. *Can. J. Chem.* **35**, 1183.
Wilson E. B. 1934. *Phys. Rev.* **45**, 706.